

Calcium Fluoride as an Internal Pressure Standard in High-Pressure/High-Temperature Crystallography

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Abstract

Cleavage plates of fluorite, CaF₂, provide a simple and sensitive pressure calibration based on variation of the cubic unit-cell volume in high-pressure/high-temperature (*PT*) single-crystal diffraction experiments, when temperature is measured independently by thermocouple. Over the range $0 \leq T \leq 500^\circ\text{C}$ and $P \leq 0.04$ Mbar (4 GPa), the temperature–pressure–volume equation of state for CaF₂ is approximately

$$\frac{\Delta V}{V_0} = 5.553 \times 10^{-5} T + 2.222 \times 10^{-8} T^2 + 2.152 \times 10^{-11} T^3 - 1.217 P - 0.00043 TP + 2.25 P^2 + 0.00078 TP^2,$$

where $\Delta V/V_0$ is the fractional change in cubic unit-cell volume from $T=0^\circ\text{C}$ and $P=0$ Mbar, T is temperature in $^\circ\text{C}$, and P is pressure in Mbar. Crystal structures of CaF₂ determined at several *PT* conditions are evidence of reversibility of single-crystal unit-cell parameters with heating and compression. Nonreversible changes occurred in observed temperature factors and extinction parameter.

Introduction

Single-crystal diffraction experiments are now possible at simultaneous high pressure and high temperature (*PT*) conditions with a *PT*, diamond-anvil cell (Hazen & Finger, 1981). A major difficulty in employing this cell is simultaneous calibration of the pressure and temperature environment of the crystal under study. In the *PT* cell, temperature calibration is based on the known thermal characteristics of a miniature resistance heater with built-in thermocouple and feedback control of power to the heating element. Pressure calibration, however, must be based on the variations of physical properties of an internal standard.

There is no optical access to the sample in the *PT* cell, so spectroscopic pressure calibration is not possible. A single-crystal, X-ray, pressure standard is a logical alternative. The ideal *PT* X-ray standard should have the following characteristics:

1. chemical and structural stability over the range of *PT* conditions to be studied;
2. no reactivity with fluid pressure medium;

3. significant unit-cell variation with *P* for calibration sensitivity;

4. reversibility (*i.e.* no hysteresis) in unit-cell dimensions following application of *P* and *T*;

5. cubic symmetry for ease of reflection identification and minimum interference with sample crystal;

6. strong diffraction intensity to minimize volume of the standard;

7. excellent cleavage for use with thin plate crystals that will uniformly shadow the sample without taking too much space.

8. a well-known *P–T*–volume equation of state.

Few compounds meet these requirements. Sodium chloride, for example, meets criteria 3 through 8, but it has been found to dissolve at elevated temperatures in fluid pressure media, including methanol–ethanol, glycerin and index-of-refraction immersion oils. Rock-salt-structure oxides, such as MgO, are relatively incompressible and thus do not meet criterion 3. One common substance that does satisfy all eight requirements is the mineral fluorite, CaF₂. This report describes the use of CaF₂ in pressure calibration for *PT* cell diffraction experiments.

Experimental

Single crystals of pure, colorless, gem-quality fluorite from Derbyshire, England, were provided by the United States National Museum of Natural History (USNM specimen number C944-1). Fluorite has perfect (111) cleavage, and may be cut into platelets of the desired size with a razor. A flat triangular plate, 150 μm on each of three edges and 15 μm thick, was used in the present investigation. The crystal was attached to one diamond-anvil face with a small dab of silicone vacuum grease, and Cargille index-of-refraction oil ($n=1.515$) was used as hydrostatic pressure fluid. The flat CaF₂ plate remained within $\pm 1^\circ$ of the diamond-anvil surface throughout the set of *PT* experiments.

Unit-cell dimensions at *P* and *T* were determined with techniques described by King & Finger (1979). Three-dimensional position and intensity data were collected with an automated, Picker, four-circle diffractometer at the eight different sets of *PT* conditions recorded in Table 1. All reflections in reciprocal space for which both incident and diffracted beams were within 36° of the central axis of the cell, and for which

$\sin \theta/\lambda < 0.68$ were collected in *PT* diamond-cell experiments; a quadrant of reciprocal space with $\sin \theta/\lambda < 1.00$ was collected in the standard experiment in air. Data were averaged yielding between 22 and 26 nonequivalent observed reflections in the *PT* cell experiments. In six of the seven *PT* cell experiments one reflection was rejected because of interference by diffraction from boron carbide elements of the cell. Refinement was accomplished by use of the least-squares program *RFINE* (Finger & Prince, 1975). Calcium fluoride is in space group *Fm3m*, with both Ca and F atoms in fixed positions. Three refined variables are the isotropic temperature factors of Ca and F, and an extinction parameter. Values of cubic unit-cell edge and volume, refined parameters, and residuals for the eight CaF_2 refinements are listed in Table 1.

Results and discussion

Equation of state of CaF_2 and pressure calibration

The *P-V-T* equation of state of CaF_2 is required if fluorite is to be used as an internal pressure standard. Thermal expansion (α) of CaF_2 (at 1 bar) has been reported by Sharma (1951), Batchelder & Simmons (1964) and Larionov & Malkin (1975). Their data yield the polynomial relationship (*T* in °C):

$$\alpha = \frac{1}{V} \left(\frac{dV}{dT} \right)_P = 5.553 \times 10^{-5} + 4.443 \times 10^{-8} T + 6.456 \times 10^{-11} T^2. \quad (1)$$

This equation is valid between 0 and 650°C. Compressibility of CaF_2 (at 0°C) has been reported by several authors, including Wong & Schuele (1967) and Ho & Ruoff (1967). Below 40 kbar the compressibility of CaF_2 is approximately (*P* in Mbar)

$$\beta_{0,P} = \frac{-1}{V} \left(\frac{dV}{dP} \right)_T = 1.217 - 4.5P. \quad (2)$$

The effect of temperature on β has been determined by Wong & Schuele (1968) and Nikanorov, Kardashev & Kas'kovich (1968):

$$\beta_{T,0} = \beta_{0,0}(1 + 0.00035T). \quad (3)$$

This formula is valid to at least 500°C.

The total volume change between ambient conditions and high *T* and *P*, represented by $\Delta V_{T,P}/V_0$, may be calculated as the sum of volume changes from ambient to *T* and room pressure, plus the volume change from high *T* to high *T* and *P*:

$$\begin{aligned} \frac{\Delta V_{T,P}}{V_0} &= \frac{V_{T,P} - V_0}{V_0} = \frac{V_{T,0} - V_0}{V_0} + \frac{V_{T,P} - V_{T,0}}{V_0} \\ &= \frac{\Delta V_1}{V_0} + \frac{\Delta V_2}{V_0}. \end{aligned}$$

The terms ΔV_1 and ΔV_2 may be calculated by integration of equations (1), (2) and (3):

$$\begin{aligned} \frac{\Delta V_1}{V_0} &= \int_0^T \alpha_{T,0} dT = 5.553 \times 10^{-5} T \\ &\quad + 2.222 \times 10^{-8} T^2 \\ &\quad + 2.152 \times 10^{-11} T^3 \end{aligned} \quad (4)$$

and

$$\begin{aligned} \frac{\Delta V_2}{V_0} &= - \int_0^P \beta_{T,P} dP \simeq - \int_0^P \left(\frac{\beta_{T,0} \beta_{0,P}}{\beta_{0,0}} \right) dP \\ &= -1.217P - 0.00043TP + 2.25P^2 \\ &\quad + 0.00078TP^2. \end{aligned} \quad (5)$$

Equations (4) and (5) represent a *T-P-V* equation of state for CaF_2 that is valid for the range 0 to 500°C and 0 to 0.04 Mbar. The functional form of this equation of state has no theoretical significance; it is an empirical polynomial fit to previous experimental *T-P-V* data. The equations are well suited to the determination of *P* if *T* and *V* are known. Equations (4) and (5) are most conveniently used in graphical form (Fig. 1), which is the pressure calibration chart now in use at the Geophysical Laboratory.

With centering of the six equivalent 220 reflections

Table 1. Refinement conditions and refined parameters for CaF_2 under several *PT* conditions

Figures in parentheses represent e.s.d.'s of least units cited.

	Conditions		Unit-cell parameters			Temperature factors		Extinction $r^* (\times 10^5)$	Residuals		Number observed ($I > 2\sigma_T$)
	<i>P</i> (kbar)†	<i>T</i> (°C)	<i>a</i> (Å)	<i>V</i> (Å ³)	$\Delta V/V_0$ (%)‡	<i>B</i> _{Ca} (Å ²)	<i>B</i> _F (Å ²)		<i>R</i> (%)	<i>wR</i> (%)	
In air	0.001	23	5.4632 (3)	163.07 (1)	0.17	0.54 (2)	0.76 (2)	0.123 (7)	0.7	0.9	34
In <i>PT</i> cell	0.001	23	5.463 (1)	163.1 (1)	0.18	0.65 (4)	0.95 (5)	0.116 (12)	1.6	1.3	26
	6.9 (10)	23	5.449 (1)	161.8 (1)	-0.62	1.01 (7)	1.14 (8)	0.069 (15)	2.5	1.9	24
	10.9 (10)	100 (5)	5.447 (1)	161.6 (1)	-0.75	1.16 (7)	1.29 (7)	0.082 (23)	2.3	1.5	22
	13.9 (10)	200 (10)	5.451 (1)	162.0 (1)	-0.50	1.34 (8)	1.59 (7)	0.089 (28)	2.8	1.6	22
	19.2 (10)	300 (10)	5.450 (1)	161.9 (1)	-0.56	1.48 (9)	1.99 (9)	0.055 (24)	2.8	1.7	21
	0.001	300 (10)	5.491 (1)	165.8 (1)	1.84	1.42 (5)	1.96 (6)	0.050 (16)	2.0	1.2	22
	0.001	23	5.461 (1)	162.9 (1)	0.06	0.96 (8)	1.15 (8)	0.058 (25)	2.8	2.0	22

† Pressure is calculated from known temperature and volume of CaF_2 (see Fig. 1).

‡ V_0 is unit-cell volume at 0°C and 1 bar (162.81 Å³).

accessible as a result of the fixed orientation of the CaF_2 standard crystal, the unit-cell volume of fluorite may be measured to approximately 1 part in 2000. The error in temperature calibration is about 10°C , which is equivalent to an additional uncertainty of 1 part in 2000 in the cell edge. The resultant uncertainty in pressure measurement (*i.e.* the pressure required to change the cell edge by approximately 0.10%) is about 1 kbar.

The CaF_2 crystal returned to its initial dimensions after more than 15 d of heating and compression, to maximum conditions of 450°C and 30 kbar. Under these experimental conditions fluorite apparently undergoes no irreversible structural change, a prime requirement for an internal pressure standard.

The third, fourth, and fifth experiments in the *PT* cell involved heating the cell without varying the spring-applied load. There was no significant variation in unit-cell volume between the second and fifth experiments because each increase in temperature was exactly balanced by an increase in pressure. Thus isovolume conditions were maintained. The *PT* cell may thus prove especially useful in studying structural variations with *P* and *T* at constant molar volume.

Temperature factors and extinction

Nonreversible changes are observed in isotropic temperature factors (B_{Ca} and B_{F}) as a result of the variation in *PT* conditions. A significant increase is observed following the application of 10 kbar at room temperature (Table 1). This effect contrasts with results of many other high-pressure structure studies (Finger & Hazen, 1979), in which temperature factors are little affected by pressure. Temperature factors increase

regularly from 23 to 100 to 200 to 300°C , but no significant change in either B_{Ca} or B_{F} is seen during release of pressure while maintaining the temperature at 300°C . Upon cooling, the temperature factors return to the values observed at 10 kbar before heating. It appears, therefore, that some irreversible change occurred in the crystal or experimental conditions in the initial application of pressure to 10 kbar. A possible explanation is that the gasket hole closed slightly between 1 bar and 10 kbar, thus resulting in an increase in shadowing of high-angle reflections. The resultant observed structure factors of higher-angle reflections would be systematically too small, and thus would lead to anomalously large temperature factors.

The isotropic extinction parameter (r^*) also underwent an irreversible change following the first application of pressure. The coefficient (Zachariasen, 1968) decreased from 1.2×10^{-6} before compression to 0.7×10^{-6} . This effect could be due to gasket shadowing or to some permanent decrease in the perfection of the sample. Changes in B_{Ca} , B_{F} , or r^* , however, do not affect the pressure calibration, which is dependent upon fluorite unit-cell volume.

Conclusions

X-ray diffraction data in the present study are the first collected at simultaneous high pressure and temperature to yield complete three-dimensional structure refinements. Future applications of *PT* crystallography will be important in resolving problems related to the nature of structures and phase transitions at non-ambient conditions. Calcium fluoride, an excellent pressure standard, will simplify the task of *PT* calibration in these experiments.

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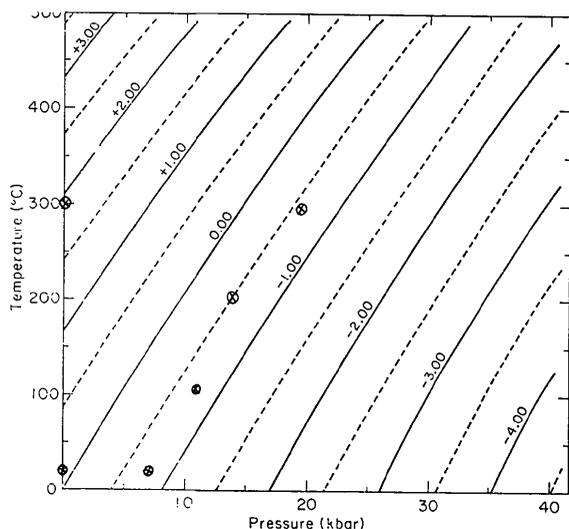


Fig. 1. Pressure-temperature-volume nomogram for calcium fluoride. If temperature and volume are known, then the pressure is uniquely defined. Symbols \otimes indicate conditions at which data collections were made.